

An optimization study for bio-removal of lead from aqueous environments by alkali modified *Polyporus Squamosus*

Şakir Yılmaz¹, Ümit Ecer^{1,*}, Tekin Şahan¹

¹ Van Yuzuncu Yil University, Faculty of Engineering, Department of Chemical Engineering, 65080 Van, Turkey, umitecer@gmail.com, ORCID: 0000-0001-9797-0959, ORCID: 0000-0002-1824-982X, ORCID: 0000-0001-8776-9338

ABSTRACT

Rapidly increasing industrialization and urbanization cause serious environmental pollution. Discharge of polluting material from various industries such as smelting, mining, ore processing, and metal plating into the environment without treatment causes serious pollution and can have dangerous effects on the environmental balance. The utilization of low-cost adsorbents from biological materials as a replacement for costly traditional methods for adsorption of heavy metal pollutants from wastewater was reviewed. This study aimed to investigate the biosorption of Pb(II) ions from aqueous solutions with NaOH-modified *Polyporus squamosus* biosorbent and optimize the biosorption conditions. Firstly, the parameters most influencing the response of the biosorption for Pb(II) (initial Pb(II) concentration (C_0), pH, temperature and biomass dose) were determined using Central Composite Design (CCD). The optimum conditions were evaluated as 60.76 mg/L, 6.3, 25 °C, and 0.23 g for C_0 , initial pH, temperature and biomass dose, respectively. From the optimum conditions, the adsorption yield and the adsorption capacity were obtained as 93.8% and 23.63 mg/g, respectively.

ARTICLE INFO

Research article

Received: 02.11.2020

Accepted: 16.12.2020

Keywords:

biosorption,
lead,
polyporus squamosus,
response surface
methodology

*Corresponding author

1. Introduction

A disadvantage arising from rapidly increasing industrialization, the presence of toxic heavy metals in aqueous environments emerges as an environmental problem that needs to be solved worldwide. Heavy metals are toxic pollutants that pose a risk to life even at very low concentrations [1]. The most common heavy metals in industrial wastewater can be listed as lead, cadmium, mercury, copper and zinc. Among these heavy metals, lead is a common metal that must be removed from industrial wastewater, as it causes serious harm to the peripheral and central nervous system of humans [2]. The permitted drinking water standard for Pb is 10 µg/L according to the World Health Organization (WHO) and 50 µg/L according to the Environmental Protection Agency (EPA) [3]. Leaving the wastewater released by the use of lead in the industrial field to the environment without any treatment increases the lead pollution in natural water resources. Pb; it is one of the raw materials widely used in oil refineries, paint, photographic materials, and battery industry. Organic and inorganic lead contamination is encountered in battery factory wastewater (2.44 mg/L), gold mining (85 mg/L), and electroplating wastewater (11.9 mg/L) [4-6]. Therefore, lead must be

removed before the wastewater can be discharged. Over the years, various methods have been used and proposed to remove heavy metals present in wastewater. The most common removal methods are coagulation, chemical precipitation, reverse osmosis, ion exchange, and adsorption/biosorption. However, each of these technologies has its disadvantages, such as high-energy requirements, production of undesirable secondary pollution, incomplete removal, low efficiency, and high costs [7, 8]. These disadvantages show that biosorption as a serious alternative technology. Biosorption is the removal of pollutants from aqueous environments using biological material [9]. Therefore, the biosorption process is increasingly considered as a potential alternative way to remove industrial pollutants. Biosorption of heavy metals onto various microbial biomasses such as fungi, algae and bacteria has been widely studied [10, 11]. The removal potential for heavy metals in industrial wastewater using biological materials is increasingly reported from different parts of the world [10, 12, 13]. Among the biological materials, fungi are one of the most frequently used biosorbents in recent years. Fungi have high potential for use in heavy metal removal due to their high surface area, abundance in nature, and being both economic and

environmentally friendly. Due to all these advantages, fungi have high importance in the treatment of wastewater [14]. Traditionally, it is difficult to observe the simultaneous effect of factors that influence a response, which requires additional experiments. With the traditional methods, one parameter is changed, while others are kept at a constant level [15, 16]. Response Surface Methodology (RSM) is the most satisfying optimization method used by researchers recently with various technologies. This method contains a collection of mathematical and statistical techniques that are beneficial for developing, optimizing, and improving processes. RSM can determine the influence of independent factors either individually or in combination with a process and is able to decrease the number of experiments necessary to analyze the process statistically for a range of factors [17]. RSM basically creates a mathematical model based on the results obtained from experimental data. It is a strong optimization tool which optimizes process conditions [14, 18]. Central composite design (CCD) in RSM with the help of Design Expert Version 7.0 (Stat Ease, USA) was used for this purpose. The statistical design can help to clarify the interaction of the various factors and define the optimum condition of the factors for biosorption/ adsorption [19]. CCD is optimal for sequential trials and provides an adequate amount of data for testing lack of fit while not confusing uncommonly large number of design points.

Due to the serious harmful effects of water contamination by heavy metals, there is an urgent need to find effective methods to eliminate such contamination. This study aimed to determine the optimum conditions for Pb(II) adsorption by NaOH treated *Polyporus squamosus*, a novel biosorbent, from aqueous solutions. For this purpose, naturally abundant and low cost *Polyporus squamosus* was modified with NaOH to enhance adsorption affinity for Pb(II) ions compared to pure *Polyporus squamosus*. The effect of independent variables (initial Pb(II) concentration (C_o , mg/L), pH, temperature (°C) and biosorbent amount (g)) were examined and optimized using central composite design (CCD). RSM, a statistical and mathematical method used to optimize the biosorption conditions, offers many advantages in terms of time and cost. Also, it supplies more data, tables, and diagrams with very few experiments.

2. Materials and methods

2.1 Materials

2.1.1 Raw biosorbent

Natural *P. Squamosus* fungi ((*Huds.*) *Fr.*) was collected from the Yüksekova area in Eastern Turkey. *P. Squamosus* fungi were washed with deionized water to remove impurities before use as biosorbent. The biomass was then dried at 60 °C and ground with a mill. It was sieved to select particles of 125 µm size and then stored in a desiccator to be treated with NaOH on the surface.

2.1.2 Chemical modification of *P. Squamosus* biosorbent

For the modification process, a certain amount of the *P. Squamosus* powder prepared previously was weighed (50 g) and treated with 500 mL of 0.1 M sodium hydroxide (NaOH) solution overnight. Then the slurry was filtered and washed with distilled water. The residues were then dried at 90 °C overnight and used for adsorption experiments.

2.1.3. Pb(II) biosorption experiment

Stock solution of Pb(II) was prepared by dissolving a certain amount of analytical grade $Pb(NO_3)_2$ (purity ≥ 99 , Sigma-Aldrich) in deionized water. The initial solution pH was set by using 0.1M NaOH and HNO_3 solutions previously available for this purpose. All tests were performed in Erlenmeyer flasks containing 100 mL of Pb (II) solution with a temperature-controlled magnetic stirrer. Biosorption experiments were completed under different conditions including initial concentration (C_o , 10–100 mg/L), initial pH (2–7.5), temperature (20-50 °C) and biomass amount (0.05-0.4 g). Samples taken after the desired contact period were filtered with a filter paper (Whatman No. 42) to remove the biosorbent. After biosorption for all solutions, the concentration of un-biosorbed Pb(II) in residual solutions were determined by utilizing an Atomic Absorption Spectrometer (AAS) (THERMO Solar AA Series spectrometer, USA). The removal percentages and adsorption amounts were calculated using Eqs. 1 and 2, respectively.

$$\% \text{ Biosorption} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e) V}{W} \quad (2)$$

where, q_e is the Pb(II) biosorption capacity (mg/g), C_i is initial and C_e is equilibrium concentration (mg/L), respectively, W is the biosorbent amount (g) and V is the volume of the solution (L).

2.1.4 Experimental design for biosorption studies

Four independent parameters (C_o , initial pH, temperature and biomass amount) were determined for the biosorption optimization of Pb(II) with NaOH-modified *P. Squamosus*. The relationship between these independent parameters and response was determined using CCD in the RSM. The total number of experiments (N) was determined by Eq. 3. Four independent parameters were designed with 3 coded values (-1, 0, +1). The actual levels and ranges are given in Table 1. The obtained experimental data were subjected to the following quadratic model to estimate the response (Eq. 4).

$$N = 2^k + 2k + 6 \quad (3)$$

$$y_p = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} x_i x_j \quad (4)$$

where, k is the number of independent parameters, y_p is the response, β_0 is constant, β_i is linear, β_{ii} is quadratic, and β_{ij} is interaction coefficients. x_i (i=1-4) are the independent parameters.

Table 1. Levels of parameters for CCD experiments.

Independent parameters	Unit	Coded	Coded and un-coded values		
			-1	0	+1
Initial conc. (C_0)	mg/L	X ₁	10	55	100
Initial pH		X ₂	2	4.75	7.5
Temperature (T)	°C	X ₃	20	35	50
Biomass amount (m)	g	X ₄	0.05	0.225	0.40

Table 2. Experimental response for CCD of Pb(II) ion removal.

Run	X ₁	X ₂	X ₃	X ₄	Biosorbed Pb(II) amount (mg/g) (Observed)	Biosorbed Pb(II) amount (mg/g) (Predicted)	ε (Predicted-Observed)
1	10 (-1)	2 (-1)	50 (+1)	0.05 (-1)	1.42	0.889	-0.531
2	10 (-1)	2 (-1)	20 (-1)	0.4 (+1)	0.129	0.588	0.459
3	55 (0)	7.5 (+1)	35 (0)	0.225 (0)	23.62	24.962	1.342
4	55 (0)	4.75 (0)	35 (0)	0.225 (0)	23.15	21.201	-1.949
5	55 (0)	4.75 (0)	20 (-1)	0.225 (0)	23.24	21.834	-1.405
6	100 (+1)	2 (-1)	50 (+1)	0.05 (-1)	1.243	1.643	0.401
7	100 (+1)	7.5 (+1)	50 (+1)	0.05 (-1)	16.75	18.201	1.459
8	10 (-1)	2 (-1)	20 (-1)	0.05 (-1)	3.68	2.791	-0.889
9	55 (0)	4.75 (0)	35 (0)	0.225 (0)	23.15	23.788	0.638
10	10 (-1)	2 (-1)	50 (+1)	0.4 (+1)	3.48	2.272	-1.207
11	100 (+1)	2 (-1)	20 (-1)	0.05 (-1)	1.432	1.284	-0.147
12	55 (0)	4.75 (0)	35 (0)	0.225 (0)	23.09	24.244	1.154
13	10 (-1)	7.5 (+1)	20 (-1)	0.05 (-1)	18.62	20.822	2.203
14	100 (+1)	2 (-1)	50 (+1)	0.4 (+1)	2.451	0.857	-1.593
15	10 (-1)	4.75 (0)	35 (0)	0.225 (0)	9.74	9.029	-0.710
16	55 (0)	4.75 (0)	35 (0)	0.225 (0)	23.52	24.303	0.783
17	100 (+1)	7.5 (+1)	50 (+1)	0.4 (+1)	16	13.681	-2.318
18	10 (-1)	7.5 (+1)	20 (-1)	0.4 (+1)	2.29	4.604	2.314
19	100 (+1)	2 (-1)	20 (-1)	0.4 (+1)	1.76	2.605	0.845
20	100 (+1)	4.75 (0)	35 (0)	0.225 (0)	23.08	22.230	-0.849
21	10 (-1)	7.5 (+1)	50 (+1)	0.4 (+1)	2.287	2.483	0.196
22	55 (0)	4.75 (0)	35 (0)	0.05 (-1)	21.45	21.248	-0.201
23	100 (+1)	7.5 (+1)	20 (-1)	0.05 (-1)	14.74	15.647	0.907
24	55 (0)	4.75 (0)	50 (+1)	0.225 (0)	22.84	21.928	-0.911
25	55 (0)	4.75 (0)	35 (0)	0.225 (0)	23.01	23.023	0.013
26	55 (0)	4.75 (0)	35 (0)	0.225 (0)	22.78	22.793	0.013
27	10 (-1)	7.5 (+1)	50 (+1)	0.05 (-1)	18.34	18.332	-0.008
28	55 (0)	2 (-1)	35 (0)	0.225 (0)	16.57	16.716	0.146
29	55 (0)	4.75 (0)	35 (0)	0.4 (+1)	13.05	13.013	-0.036
30	100 (+1)	7.5 (+1)	20 (-1)	0.4 (+1)	15	14.880	-0.119

3. Results and discussion

3.1. RSM modelling and ANOVA analysis

The effect of independent parameters (C_0 , initial pH, temperature, and biomass amount) on the biosorption amount was examined and optimized in a batch system. The purpose of optimization with CCD is to determine the interaction between parameters affecting the response with fewer experiments and thus to easily assign the optimum values of the parameters. For the optimization of Pb(II) biosorption, 30 batch experiments were performed and the obtained responses (amount of biosorption) are given in Table 2. Second-order regression models (with and without code) obtained from CCD for Pb (II) biosorption are given in Eqs. 4 and 5.

$$\begin{aligned} \text{Biosorbed Amount (mg/g)(uncoded)} = & -11.15221 + 0.27816[C_o] + 5.98277[\text{pH}] - 0.017148[T] \\ & + 73.25179[m] + 0.011503[C_o][\text{pH}] + 2.50370 \text{E-} 004[C_o][T] + 0.27714[C_o][m] + 1.71818 \text{E-} 003[\text{pH}][T] \\ & - 4.27506[\text{pH}][m] + 0.13710[T][m] - 3.30759 \text{E-} 003[C_o]^2 - 0.39839[\text{pH}]^2 - 3.01598 \text{E-} 004[T]^2 - 191.27705[m]^2 \end{aligned} \tag{4}$$

$$\begin{aligned} \text{Biosorbed Amount (mg/g)(coded)} = & +23.11 + 1.80[X_1] + 5.30[X_2] + 0.22[X_3] - 2.29[X_4] + 1.42[X_1X_2] + 0.17[X_1X_3] \\ & + 2.18[X_1X_4] + 0.071[X_2X_3] - 2.06[X_2X_4] + 0.36[X_3X_4] - 6.70[X_1]^2 - 3.01[X_2]^2 - 0.068[X_3]^2 - 5.86[X_4]^2 \end{aligned} \tag{5}$$

Analysis of variance (ANOVA) was used to verify the significance of the second-order regression model obtained. ANOVA for regression parameters of the quadratic model obtained from CCD for the biosorption of Pb (II) on NaOH-P. *squamosus* is presented in Table 3. The *prob > F* (>0.0001) value shows that the second-order quadratic model is significant. The high value of the coefficient of determination ($R^2 = 0.947$) indicates that 94.7% of the variability in the

response is explained by the model [20]. *p*-value was employed to identify the significance of terms, which are considered as significant to the predicted response when $p < 0.05$. From the ANOVA result, X_1, X_2, X_4 (linear terms), X_1X_4, X_2X_4 (interaction terms), X_1^2 , and X_4^2 (quadratic terms) were significant ($p < 0.05$) for the predicted response. The other terms in Table 3 have little effect on the model equation, but even these effects are important [21].

Table 3. Analysis of variance regression model for Pb(II) biosorption by using NaOH-modified *Polyporus squamosus*.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2287.220939	14	163.3729242	19.05933073	< 0.0001	significant
X ₁ -Initial conc.	58.57227222	1	58.57227222	6.833129256	0.0195	
X ₂ -pH	506.4895736	1	506.4895736	59.08783443	< 0.0001	
X ₃ -Temperature	0.853688889	1	0.853688889	0.099592628	0.7567	
X ₄ -Biomass Amount	94.43044356	1	94.43044356	11.01639739	0.0047	
X ₁ X ₂	32.421636	1	32.421636	3.782356755	0.0708	
X ₁ X ₃	0.456976	1	0.456976	0.053311507	0.8205	
X ₁ X ₄	76.2129	1	76.2129	8.89111139	0.0093	
X ₂ X ₃	0.08037225	1	0.08037225	0.009376347	0.9241	
X ₂ X ₄	67.72467025	1	67.72467025	7.900861758	0.0132	
X ₃ X ₄	2.07216025	1	2.07216025	0.241741327	0.6301	
X ₁ ²	116.2316119	1	116.2316119	13.55975443	0.0022	
X ₂ ²	23.51851937	1	23.51851937	2.743705796	0.1184	
X ₃ ²	0.01193096	1	0.01193096	0.001391884	0.9707	
X ₄ ²	88.90580096	1	88.90580096	10.37188428	0.0057	

Figure 1a shows normal % probability versus residuals. The normal probability plot is a graphical technique to identify

whether or not a data set is approximately normally distributed. Since the points on the graph are observed as a

straight line, it can be concluded that the residuals are normally distributed and data transformation is not required. For this reason, it was concluded that the estimation of the experimental data obtained from the second-order model was quite significant [22]. Generally, it is important to check that the proposed model provides an adequate approach to the actual system. If the recommended model does not show sufficient fit, examination, and optimization of the fitted response surface is likely to give misleading results. Residuals play a significant role in evaluating model adequacy. Figure 1b shows that the residuals were randomly distributed between ± 3 . It can be concluded that the results obtained are compatible with the experimental data estimated using the quadratic equation.

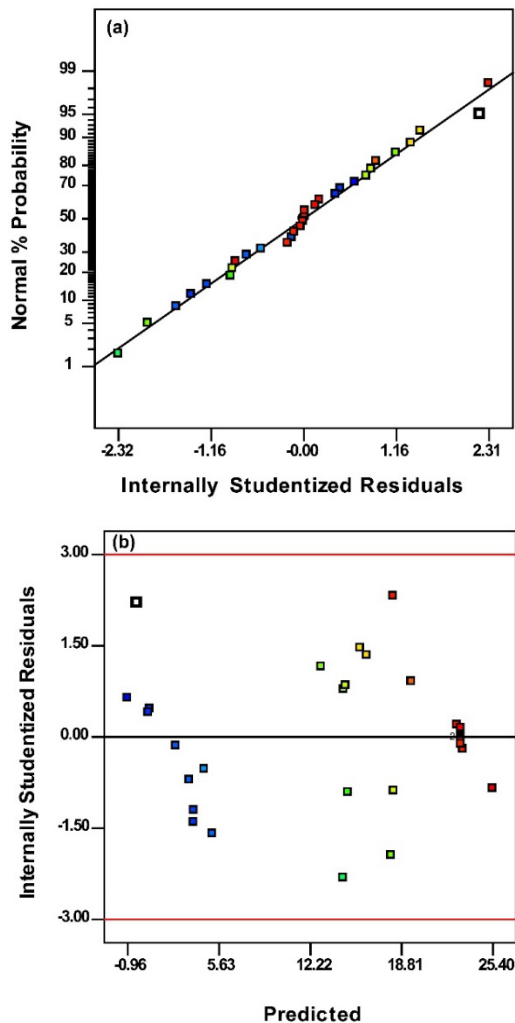


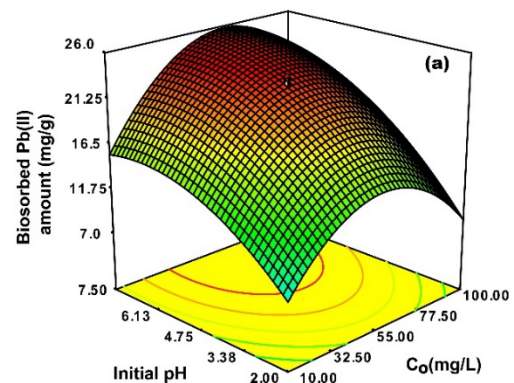
Figure 1 a) Validation of the prediction of Pb(II) biosorption residuals versus normal % probability and b) Residuals versus predicted values.

3.2. Effects of process variables on biosorption capacity

Initial pH and C_0 play a significant role in the biosorption process of heavy metal ions (Figure 2). In this work, the

biosorption of Pb(II) ions on NaOH-*P. squamosus* was studied at different pH levels ranging from 2.0 to 7.5. Removal of Pb (II) ions increased by increasing initial pH from 2.0 to 6.0 (Figure 2a). With the initially increasing pH, the active binding sites on the surface of NaOH-*P. squamosus* become negatively charged and electrostatic attraction occurs between the positively-charged Pb (II) ions and these negatively-charged groups. This conclusion can be demonstrated as the reason for the increase in Pb(II) adsorption. When the initial pH was approximately 6.5, more than 90% of the Pb(II) ions in solution were biosorbed by NaOH-*P. squamosus*. The decrease in Pb (II) biosorption at increasing initial pH values can be attributed to the separation of functional groups on NaOH-*P. squamosus* and the change in surface charge. One of the most significant reasons for this is that Pb(II) ions can precipitate as $Pb(OH)_2$ solid that does not dissolve at high pH [18]. The solution pH not only affects the charges on the adsorbent surface but also affects the ionization of the solute or inhibits ions. Therefore, initial metal solution pH values that are too high should be avoided as they may cause the precipitation of metal complexes and interfere with the separation between adsorption and precipitation [23, 24].

Adsorption experiments were conducted for various Pb(II) concentrations ranging from 10 to 100 mg/L using NaOH-*P. squamosus* to study the influence of C_0 on biosorption. The results given in Figure 2a show that Pb(II) biosorption increased with rising C_0 . The biosorption capacity of NaOH-*P. squamosus* quickly increased by increasing C_0 from 10 to 55 mg/L while no change was recorded at higher initial Pb(II) concentrations and a maximum level was approximately reached at 60.0 mg/L. These results show that the pores of NaOH-*P. squamosus* were completely full after a particular period and after that, increasing the metal concentration didn't have a significant effect on biosorption of Pb(II) ions [25, 26]. In addition, the rapid adsorption in the first stage may be due to the presence of a larger surface area, but the adsorption rate decreases due to the occupation of surface areas after adsorption begins [27].



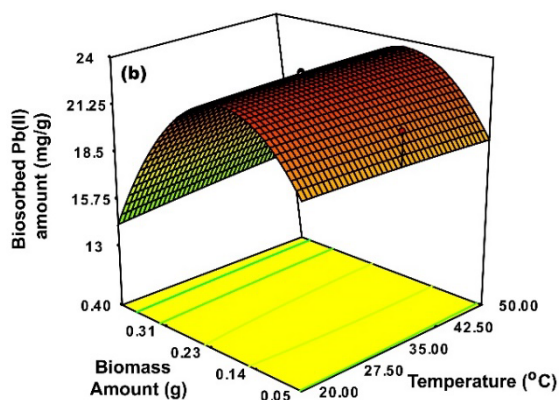


Figure 2. Simultaneous effects of a) initial concentration (C_0) and initial pH and b) temperature and biomass dosage on Pb(II) biosorption

The biomass amount is another important parameter, which influences the extent of removal from the solution, and so the effect as shown in Figure 2b. The increase in the dosage of the adsorbent is very effective in heavy metal adsorption. Results obtained from this study describe the adsorption of Pb(II) which increases rapidly when the dose of NaOH-*P. squamosus* powder is increased from 0.04 to 0.5 g; further explained by the large availability of surface area at higher concentrations of adsorbent. This study showed that the optimum biosorbent dose required for maximum adsorption was 0.22 g. Above the optimum amount, the removal efficiency did not change with increasing biomass amount. As expected, the adsorption yield increased by increasing the biomass amount for a given C_0 , because, for constant C_0 , increasing biomass amount supplies a larger surface area or more biosorption sites. On the other hand, when the biomass amount increased, the amount adsorbed per unit mass of biosorbent decreased. The reduction in biosorption capacity with a rise in the biomass amount is substantially due to the increase in free biosorption sites for the biosorption reaction [28, 29].

One of the important parameters in biosorption processes is temperature. According to the biosorption theory, adsorption is reduced as molecules adsorbed on the surface at high temperatures tend to desorb from the surface [30]. This work was carried out over a temperature range of 20 °C to 50 °C. The optimum temperature was found to be 20 °C, as shown in Figure 2b. The results obtained show that the increased temperature had an adverse effect on the biosorption capacity. Based on that fact, one may say that Pb(II) biosorption by NaOH-*P. squamosus* is an exothermic process [10, 31].

3.3. Determination of Optimum Biosorption Conditions

For the optimization procedure, the numerical optimization operation in RSM was used to determine optimum conditions for Pb(II) biosorption onto NaOH-*P. squamosus*. With numerical optimization, the optimum values for the response

and independent parameters can be identified. For this, each parameter can be selected in the target, minimum, maximum, or range in order to achieve an optimal output for a set of conditions. The main goal to be achieved in the optimization process is to determine the optimum points of the parameters that affect Pb (II) removal by NaOH-*P. squamosus*. While the response was selected as "maximize" to reach the highest value, the independent variables were arranged according to the entire studied range. The optimum values were determined as 60.76 mg/L, 6.3, 25 °C, and 0.23 g for C_0 , pH, T (°C), and biomass dosage (g), respectively, and these values were confirmed by obtained data. Under these optimum conditions, the maximum biosorbed Pb(II) amount was found to be 25.68 mg/g and biosorption yield was calculated to be 97.23%. To confirm the validity of the proposed model equation for Pb(II) biosorption by NaOH-*P. squamosus*, several tests were made with the optimum conditions obtained by the program. Based on the experimental results, biosorbed Pb(II) amount was obtained to be 24.39 mg/g, indicating that this result was fairly close to the predicted value obtained by the model at the optimum points.

The comparison between the biological material we used and some materials used in the literature is shown in Table 4. It can be said that NaOH-*P. squamosus* is a natural biosorbent with higher sorption capability than some other biosorbents/adsorbents. In addition, NaOH-*P. squamosus* waste does not pollute the environment after the biosorption process. Due to these properties, it is a biosorbent with high potential to remove heavy metals from aqueous environments. In order to understand the importance of the modification process, experiments were carried out using pure *P. squamosus* under the optimum conditions obtained. Under these conditions, the maximum amount of biosorbed Pb(II) was 12.68 mg/g. In addition, the biosorption efficiency was calculated as 67.23%. These results show that NaOH-modified *P. squamosus* significantly increased the removal of Pb(II) ions.

Table 4. Comparison of biosorption capacity of NaOH-*P. squamosus* for Pb(II) ions with different biosorbents/adsorbents

Biosorbent / Adsorbent	%Pb(II) adsorption / biosorption	Pb(II) adsorption / biosorption amount	Ref.
<i>P. squamosus</i>	89.4	13.65	[10]
Activated carbon prepared from coconut shell	96	26.5	[32]
Litchi pericarp	99.97	163.93	[33]
Banana peels	85.3	2.18	[7]
Pumice	88.49	7.46	[34]
MWCNTs	75.3	91	[35]
Oryza sativa L. husk	98.11	8.60	[36]
NaOH- <i>P. squamosus</i>	97.23	25.68	This work

4. Conclusions

In this study, the effects of the initial conc.(C₀), initial pH, temperature and biomass amount on removal were investigated using CCD in RSM for biosorption of Pb(II) from wastewater on NaOH-*P. squamosus*. The results indicated a high correlation among the predicted and experimental values. With the quadratic model obtained from CCD, the optimum biosorption conditions were determined as initial Pb(II) concentration 60.76 mg/L, initial pH 6.3, temperature 25 °C and biomass amount 0.23 g. At these optimum conditions, the optimum biosorbed Pb(II) amount and biosorption yield were found to be 25.68 mg/g and 97.23%, respectively. In addition, the adsorption capacity of *P. squamosus* modified with NaOH increased significantly compared to pure *P. squamosus*. Accordingly, the present results indicate that NaOH-*P. squamosus* is a green technology can be used for the biosorption of heavy metals from wastewater.

Acknowledgments

We would like to thank Prof. Dr. Yusuf Uzun (Van Yuzuncu Yil University) for providing the biosorbent used in this study.

References

- [1]. Garg U., Kaur M.P., Jawa G.K., Sud D., Garg V.K., "Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass", *Journal of Hazardous Materials*, 154, (2008), 1149-1157.
- [2]. Liao S.-W., Lin C.-I., Wang L.-H., "Kinetic study on lead (II) ion removal by adsorption onto peanut hull ash", *Journal of the Taiwan Institute of Chemical Engineers*, 42, (2011), 166-172.
- [3]. Gupta V.K., Ali I., "Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste", *Journal of Colloid and Interface Science*, 271, (2004), 321-328.
- [4]. Poonam, Bharti S.K., Kumar N., "Kinetic study of lead (Pb²⁺) removal from battery manufacturing wastewater using bagasse biochar as biosorbent", *Applied Water Science*, 8, (2018), 119.
- [5]. Yahya M.D., Yohanna I., Auta M., Obayomi K.S., "Remediation of Pb (II) ions from Kagara gold mining effluent using cotton hull adsorbent", *Scientific African*, 8, (2020), e00399.
- [6]. Kara A., Üstün G.E., Akal Solmaz S.K., Demirbel E., "Removal of Pb(II) Ions in Fixed-Bed Column from Electroplating Wastewater of Bursa, an Industrial City in Turkey", *Journal of Chemistry*, 2013, (2013), 953968.
- [7]. Anwar J., Shafique U., Waheed uz Z., Salman M., Dar A., Anwar S., "Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana", *Bioresource Technology*, 101, (2010), 1752-1755.
- [8]. Yang X., Zhao Z., Yu Y., Shimizu K., Zhang Z., Lei Z., Lee D.-J., "Enhanced biosorption of Cr(VI) from synthetic wastewater using algal-bacterial aerobic granular sludge: Batch experiments, kinetics and mechanisms", *Separation and Purification Technology*, 251, (2020), 117323.
- [9]. Coday B.D., Xu P., Beaudry E.G., Herron J., Lampi K., Hancock N.T., Cath T.Y., "The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams", *Desalination*, 333, (2014), 23-35.
- [10]. Ecer U., Şahan T., "A response surface approach for optimization of Pb (II) biosorption conditions from aqueous environment with *Polyporus squamosus* fungi as a new biosorbent and kinetic, equilibrium and thermodynamic studies", *Desalination and Water Treatment*, 102, (2018), 229-240.
- [11]. Li X., Xu H., Gao B., Shi X., Sun Y., Wu J., "Efficient biosorption of Pb(II) from aqueous solutions by a PAH-degrading strain *Herbaspirillum chlorophenicum* FA1", *Journal of Industrial and Engineering Chemistry*, 57, (2018), 64-71.
- [12]. Bano A., Hussain J., Akbar A., Mehmood K., Anwar M., Hasni M.S., Ullah S., Sajid S., Ali I., "Biosorption of heavy metals by obligate halophilic fungi", *Chemosphere*, 199, (2018), 218-222.
- [13]. Shi L., Deng X., Yang Y., Jia Q., Wang C., Shen Z., Chen Y., "A Cr (VI)-tolerant strain, *Pisolithus* sp1, with a high accumulation capacity of Cr in mycelium and highly efficient assisting *Pinus thunbergii* for phytoremediation", *Chemosphere*, 224, (2019), 862-872.
- [14]. Şahan T., Ceylan H., Şahiner N., Aktaş N., "Optimization of removal conditions of copper ions from aqueous solutions by *Trametes versicolor*", *Bioresource Technology*, 101, (2010), 4520-4526.
- [15]. Karri R.R., Sahu J.N., "Modeling and optimization by particle swarm embedded neural network for adsorption of zinc (II) by palm kernel shell based activated carbon

- from aqueous environment", *Journal of Environmental Management*, 206, (2018), 178-191.
- [16]. Şahan T., "Application of RSM for Pb(II) and Cu(II) adsorption by bentonite enriched with SH groups and a binary system study", *Journal of Water Process Engineering*, 31, (2019), 100867.
- [17]. Jaafari J., Yaghmaeian K., "Optimization of heavy metal biosorption onto freshwater algae (*Chlorella coloniales*) using response surface methodology (RSM)", *Chemosphere*, 217, (2019), 447-455.
- [18]. Ecer Ü., Yılmaz Ş., Şahan T., "Highly efficient Cd(II) adsorption using mercapto-modified bentonite as a novel adsorbent: an experimental design application based on response surface methodology for optimization", *Water science and technology : a journal of the International Association on Water Pollution Research*, 78, (2018), 1348-1360.
- [19]. Chowdhury S., Chakraborty S., Saha P.D., "Response surface optimization of a dynamic dye adsorption process: a case study of crystal violet adsorption onto NaOH-modified rice husk", *Environmental Science and Pollution Research*, 20, (2013), 1698-1705.
- [20]. Mona S., Kaushik A., Kaushik C.P., "Biosorption of reactive dye by waste biomass of *Nostoc linckia*", *Ecological Engineering*, 37, (2011), 1589-1594.
- [21]. Peng Y., Sun Y., Sun R., Zhou Y., Tsang D.C.W., Chen Q., "Optimizing the synthesis of Fe/Al (Hydr)oxides-Biochars to maximize phosphate removal via response surface model", *Journal of Cleaner Production*, 237, (2019), 117770.
- [22]. Hasan S.H., Srivastava P., Talat M., "Biosorption of Pb(II) from water using biomass of *Aeromonas hydrophila*: Central composite design for optimization of process variables", *Journal of Hazardous Materials*, 168, (2009), 1155-1162.
- [23]. Kubilay Ş., Gürkan R., Savran A., Şahan T., "Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite", *Adsorption*, 13, (2007), 41-51.
- [24]. Ahmed Z., Wu P., Jiang L., Liu J., Ye Q., Yang Q., Zhu N., "Enhanced simultaneous adsorption of Cd(II) and Pb(II) on octylamine functionalized vermiculite", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 604, (2020), 125285.
- [25]. Forghani M., Azizi A., Livani M.J., Kafshgari L.A., "Adsorption of lead(II) and chromium(VI) from aqueous environment onto metal-organic framework MIL-100(Fe): Synthesis, kinetics, equilibrium and thermodynamics", *Journal of Solid State Chemistry*, 291, (2020), 121636.
- [26]. Menezes J.M.C., da Silva Bento A.M., da Silva J.H., de Paula Filho F.J., da Costa J.G.M., Coutinho H.D.M., Pereira Teixeira R.N., "Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by *Caryocar coriaceum* Wittm barks", *Chemosphere*, 261, (2020), 128144.
- [27]. Idris M.N., Ahmad Z.A., Ahmad M.A., "Adsorption equilibrium of malachite green dye onto rubber seed coat based activated carbon", *Int J Basic Appl Sci*, 11, (2011), 38-43.
- [28]. Mousavi H., Hosseynifar A., Jahed V., Dehghani S., "Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent", *Brazilian Journal of Chemical Engineering*, 27, (2010), 79-87.
- [29]. Gapusan R.B., Balela M.D.L., "Adsorption of anionic methyl orange dye and lead(II) heavy metal ion by polyaniline-kapok fiber nanocomposite", *Materials Chemistry and Physics*, 243, (2020), 122682.
- [30]. Bhatti H.N., Khalid R., Hanif M.A., "Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge", *Chemical Engineering Journal*, 148, (2009), 434-443.
- [31]. Albalasmeh A., Gharaibeh M.A., Mohawesh O., Alajlouni M., Quzaih M., Masad M., El Hanandeh A., "Characterization and Artificial Neural Networks Modelling of methylene blue adsorption of biochar derived from agricultural residues: Effect of biomass type, pyrolysis temperature, particle size", *Journal of Saudi Chemical Society*, 24, (2020) 811-823.
- [32]. Sekar M., Sakthi V., Rengaraj S., "Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell", *Journal of Colloid and Interface Science*, 279, (2004), 307-313.
- [33]. Sun S., Yang J., Li Y., Wang K., Li X., "Optimizing adsorption of Pb(II) by modified litchi pericarp using the response surface methodology", *Ecotoxicology and Environmental Safety*, 108, (2014), 29-35.
- [34]. Şahan T., Öztürk D., "Investigation of Pb(II) adsorption onto pumice samples: application of optimization

method based on fractional factorial design and response surface methodology", *Clean Technologies and Environmental Policy*, 16, (2014), 819-831.

[35]. Wang H., Zhou A., Peng F., Yu H., Yang J., "Mechanism study on adsorption of acidified

multiwalled carbon nanotubes to Pb(II)", *Journal of Colloid and Interface Science*, 316, (2007), 277-283.

[36]. Zulkali M.M.D., Ahmad A.L., Norulakmal N.H., "Oryza sativa L. husk as heavy metal adsorbent: Optimization with lead as model solution", *Bioresource Technology*, 97, (2006), 21-25.

Desalination and Water Treatment